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Modern Thermodynamic Theory of Thermoelectricity

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2.1 Introduction

Thermodynamics is an efficient means of finding most general regularities in the theory of thermoelectricity.

In 1854, W. Thomson¹ using equilibrium thermodynamics established the interrelation between three thermoelectric effects that arise in a thermocouple thermoelectric circuit with the legs of individual isotropic media (Figure 2.1) in the form of relationships

$$d\Pi/dT - \alpha - \tau = 0 \quad (2.1)$$

$$d\Pi/dT - \Pi/T - \tau = 0 \quad (2.2)$$

where α is the Seebeck coefficient, Π is the Peltier coefficient, and τ is the Thomson coefficient. Equation 2.1 and Equation 2.2 imply two relationships of frequent use in thermoelectricity:

$$\Pi = \alpha T \text{ is the first Thomson relationship} \quad (2.3)$$

$$\tau = T(\partial\alpha/\partial T) \text{ is the second Thomson relationship} \quad (2.4)$$

It is common knowledge today that a rigorous thermodynamic theory of thermoelectricity can be constructed only on the basis of a nonclassical, more general theory of macroscopic description of nonequilibrium processes called nonequilibrium thermodynamics or thermodynamics of irreversible processes.²⁻⁷

Stated below are the basic concepts of modern nonequilibrium thermodynamics as applied to thermoelectricity, which make possible specification and generalization of the Thomson theory not only

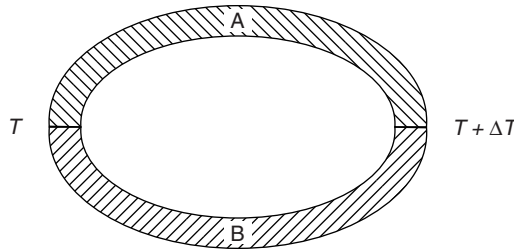


FIGURE 2.1 Thermocouple thermoelectric circuit with the legs of individual isotropic media A and B. Thermocouple junctions are at temperatures T and $T + \Delta T$.

for thermocouple power converters, but also for thermoelectric media of any complexity used in them, generalization of fundamental thermoelectric relationships, discovery of new thermoelectric effects, and formulation of general efficiency criteria for materials used in thermoelectric devices.

2.2 Nonequilibrium Thermodynamics: General Concepts

This is a reminder in brief the concepts of classical thermodynamics.

The first law of thermodynamics is a concept expressing the law of conservation of energy whereby the quantity of system-absorbed heat δQ can be expressed as the relationship

$$\delta Q = dU + \delta A - \mu dn \quad (2.5)$$

where dU is a change in internal system energy, δA is work performed by the system against external forces, μ is system chemical potential, and dn is a change in the number of particles in the system.

The second law of thermodynamics, whereby

$$TdS \geq \delta Q \quad (2.6)$$

where the equality sign is related to reversible, and nonequality sign, to irreversible processes; T is absolute temperature, dS is total differential of state function S which is commonly called entropy. The classical theory of thermodynamics of reversible processes outlines only the idealized processes. For real, i.e., nonequilibrium processes (such as heat transfer, electric current flow), classical theory provides only the inequalities of 2.6 type, indicating the possible evolution of these processes.

A decisive step for the creation of nonequilibrium thermodynamics was made in 1931 by Onsager.⁸ He formulated for thermodynamics a new general principle of minimum energy dissipation. Besides, Onsager put forward a partial principle that was a generalization of Ohm's and Fourier equations. According to this partial principle, irreversible processes can be described by linear differential equations with constant coefficients, L_{ik} , for which the symmetry relations of the type $L_{ik} = L_{ki}$ are satisfied. The Onsager principle was of considerable importance in the development of thermodynamics of irreversible processes.

Unlike Onsager, Prigozhin⁴ put forward a new, also general principle for thermodynamics, namely the principle of minimum entropy production, which proved to be more convenient for the solution of practical tasks than the Onsager principle. This principle determines a criterion for thermodynamic system evolution whereby under nonequilibrium conditions held constant a thermodynamic system evolves to a steady-state having relative stability and characterized by a minimum rate of entropy production. The most essential conclusion in the Prigozhin theory is that with increasing the degree of system state nonequilibrium, for example, with increasing thermodynamic forces, the state of homogeneous chaos becomes unsteady, kinetic-phase transitions occur in the system, and ordered dissipation structures are formed providing a higher entropy production rate as compared to the chaotic state. Numerous investigations show that this regularity is universal, valid for various-complexity systems.^{9,10}

At the present time linear and nonlinear versions are recognized in nonequilibrium thermodynamics. The best developed is a linear nonequilibrium thermodynamics with its prime objective to study nonequilibrium processes for near-equilibrium states.

In thermodynamics of irreversible processes the systems with nonequilibrium processes are regarded as continuous media, and their state parameters as field variables, i.e., continuous coordinate and time functions.

For a macroscopic description of nonequilibrium processes the following method is used: a system is represented as consisting of elementary volumes (Figure 2.2), although big enough to comprise a very large number of particles. The state of each elementary volume in a medium is characterized by temperature, pressure, and other thermodynamic parameters depending on coordinates and time, i.e., it is assumed that this element is actually in the state of local equilibrium even when the system in general is thermally nonequilibrium. This assumption is called the principle of local equilibrium.

Quantitatively, the nonequilibrium processes in this method are described by balance equations for elementary volumes based on the laws of conservation of mass, momentum, and energy, entropy balance equations, as well as phenomenological equations of the processes in question that express mass, momentum, electric current, and energy flows in terms of the gradients of thermodynamic parameters.

The methods of theory of irreversible processes allow formulating for nonequilibrium processes the first and second laws of thermodynamics in a local form, as well as obtaining from the general principles a complete set of energy, mass, momentum, and entropy transport equations, i.e., equations for the description of thermoelectric phenomena, hydrodynamics, thermal conductivity, diffusion, etc. These equations are fundamental for nonequilibrium thermodynamics. In thermoelectricity, where mass and momentum transport is not essential, local equations of energy balance and entropy are of basic importance.

The law of conservation of energy for volume elements is the first law of thermodynamics in the theory of irreversible processes. Here one should take into account that total unit energy is composed of unit kinetic, unit potential energy in the field of forces \mathbf{F}_k , unit internal energy u , which is the energy of thermal motion of particles, and the average interaction energy. Between them the balance equation for u is of the form

$$\rho(dpu/dt) = -\text{div}(\rho u \mathbf{v} + q) - \sum_{\alpha\beta} P_{\alpha\beta}(\partial v_{\alpha}/\partial x_{\beta}) + \sum_k \mathbf{J}_k \mathbf{F}_k \quad (2.7)$$

where q is density, \mathbf{v} is mass transport velocity, and in so doing, the rate of change in momentum density per one particle $\partial \rho u / \partial t$ is determined by the divergence of internal energy flows $\rho u \mathbf{v}$ and heat flow q , and the work of internal mechanical stresses $\sum_{\alpha\beta} P_{\alpha\beta}(\partial v_{\alpha}/\partial x_{\beta})$ and external forces $\sum_k \mathbf{J}_k \mathbf{F}_k$.

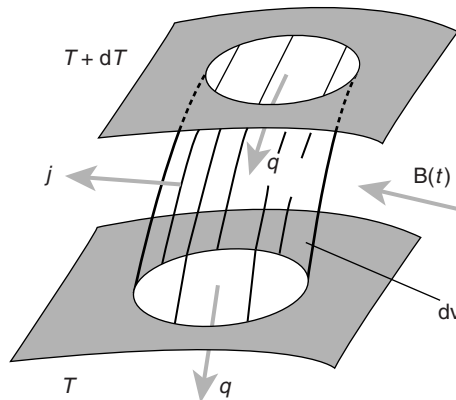


FIGURE 2.2 Elementary volume dV of thermoelectric medium considered in nonequilibrium thermodynamics. This volume is also used in local thermoelement models.

Entropy balance equation. In thermodynamics of irreversible processes it is assumed that the entropy of volume unit s (local entropy) is the same function of internal energy u , unit volume $v = 1/\rho$ and concentration c , as in the state of full equilibrium; hence, regular equalities of classical thermodynamics hold true for it. These concepts together with the laws of conservation of mass, momentum, and energy permit finding the entropy balance equation

$$\rho(ds_s/dt) = -\text{div } \mathbf{J}_s + \sigma_s \quad (2.8)$$

where σ_s is unit local entropy production per unit time, \mathbf{J}_s is entropy flow density expressed in terms of heat flow density, diffusion density, and that part of stress tensor which is related to nonequilibrium processes (i.e., in terms of elastic stress tensor $\Pi_{\alpha\beta}$). Entropy (in contrast to mass, energy, and momentum) is not retained, but increases with time in volume element due to irreversible processes with the rate of σ_s increase. Besides, entropy can change on its leaking into or out of volume element, which is not related to irreversible processes. The positive character of entropy production $\sigma \geq 0$ is expressed in thermodynamics of irreversible processes by the law of entropy increase.

Entropy production σ_s is determined only by irreversible processes (such as diffusion, thermal conductivity, viscosity) and is equal to

$$\sigma_s = \sum_i \mathbf{J}_i \mathbf{X}_i \quad (2.9)$$

where \mathbf{J}_i are flows (for example, diffusion flow \mathbf{J}_c , heat flow q , elastic stresses tensor $\Pi_{\alpha\beta}$), and \mathbf{X}_i are their conjugate thermodynamic forces, i.e., gradients of thermodynamic parameters causing a deviation from equilibrium state. To obtain in thermodynamics of irreversible processes a closed set of equations describing nonequilibrium processes, the flows of physical quantities should be expressed by phenomenological equations in terms of thermodynamic forces.

Phenomenological equations. Thermodynamics of irreversible processes proceeds on the assumption that with low system deviations from thermodynamic equilibrium the arising flows are linearly dependent on thermodynamic forces and described by phenomenological equations of the type

$$\mathbf{J}_i = \sum_k L_{ik} \mathbf{X}_k \quad (2.10)$$

where L_{ik} are kinetic (phenomenological) or transport coefficients. In direct processes thermodynamic force \mathbf{X}_k brings about flow \mathbf{J}_k , for example, temperature gradient brings about heat flow (thermal conductivity), concentration gradient — substance flow (diffusion), velocity gradient — momentum flow (that determines viscosity), electric field — electric current (electric conductivity). Such processes are characterized by kinetic coefficients, proportional to coefficients of thermal conductivity, diffusion, viscosity, and electric conductivity. These coefficients are also called kinetic coefficients or transport coefficients. Thermodynamic force \mathbf{X}_k can induce thermoelectric current, and electrochemical potential gradient — heat flow (Peltier effect). Such processes are called cross-flow or overlapping effects. They are characterized by coefficient L_{ik} with $i \neq k$. With regard for phenomenological equations, entropy production is equal to

$$\sigma_s = \sum_{i,k} \mathbf{X}_i L_{ik} \mathbf{X}_k \geq 0 \quad (2.11)$$

In steady-state the value σ_s is minimum under assigned external conditions preventing from establishment of equilibrium. This statement is known as Prigogin's theorem. In the state of thermodynamic equilibrium, $\sigma_s = 0$. In the above-discussed examples thermodynamic parameters are continuous coordinate functions. Nonequilibrium systems are possible where thermodynamic parameters are changed abruptly (heterogeneous systems), for example, electron gas in metal thermocouple or gases in vessels connected with a capillary or membrane. If temperatures T and chemical potentials μ of components on both sides of the thermocouple junction or membrane between the vessels are not equal

($T_1 > T_2$ and $\mu_1 > \mu_2$), thermodynamic forces ($X_n = 1/T_2 - 1/T_1$, $X_m = \mu_2/T_2 - \mu_1/T_1$) bring about particle and energy flows ($\mathbf{J}_m = L_{11}\mathbf{X}_m + L_{12}\mathbf{X}_n$, $\mathbf{J}_n = L_{21}\mathbf{X}_m + L_{22}\mathbf{X}_n$) between the heterogeneous system parts, creating thermal difference in pressures. In these examples the flows and thermodynamic forces are scalars and accordingly such processes are called scalar. In thermoelectricity the flows and thermodynamic forces are vectors; hence they are called vector processes. In hydrodynamics at shear viscosity thermodynamic forces and flows are tensors.

Thermodynamics of irreversible processes provides a theoretical basis for the investigation of open systems. It offers explanation of many nonequilibrium phenomena in conductors, including thermoelectric, galvanomagnetic, and galvanothermomagnetic phenomena.

According to the thermodynamics of irreversible processes,²⁻⁶ the basic equation of thermodynamics for quasistatic processes is applicable to parts of physical system (medium) being in local equilibrium

$$TdS = dU + \delta A - \sum_r \mu_r dn_r \quad (2.12)$$

that follows from Equation 2.5 and Equation 2.6.

Thermodynamic flow caused by thermodynamic forces X_k is related to them by a linear law (Equation 2.10) where kinetic coefficients L_{ik} describing medium properties are assumed to be known.

It should be noted that even in modern publications,⁷ a linear law of type shown in Equation 2.10 is not infrequently written in a simplified form, suitable only for isotropic medium. However, for a full and correct description it should be assumed that thermodynamic flows and forces are components of three-dimensional vectors, and kinetic coefficients — components of second-rank tensors so that summation limit in Equation 2.10 is equal to the number of all vector components of thermodynamic forces.

If thermodynamic flows and forces are selected such that entropy production rate σ_s can be represented as Equation 2.11, for kinetic coefficients the Onsager symmetry principle holds true:

$$L_{ik} = L_{ki} \quad (2.13)$$

In the presence of a magnetic field bold dependence of kinetic coefficients more general relations hold true:

$$L_{ik}(\mathbf{B}) = L_{ki}(-\mathbf{B}) \quad (2.14)$$

where \mathbf{B} is magnetic induction vector.

As a rule, a relation between electric field \mathbf{E} , electric current density \mathbf{j} , and conducting medium property (electric resistivity ρ), as well as a relation between temperature gradient ∇T , heat flow density \mathbf{q} , and medium thermal conductivity κ is found from Ohm's and Fourier laws, which are of the form

$$\mathbf{E} = \rho \mathbf{j} \quad (2.15)$$

$$\mathbf{q} = -\kappa \nabla T \quad (2.16)$$

Equation 2.15 and Equation 2.16 are valid for the cases when either electric processes or thermal processes alone occur in a medium; therefore these equations in principle cannot describe thermoelectric effects for which the simultaneous existence and interaction of thermal and electric processes is important.

2.3 Thermodynamic Theory of Thermoelectricity

2.3.1 Generalized Ohm's and Fourier Laws

Consider generalizations of Equation 2.15 and Equation 2.16 for thermoelectric phenomena.

The application of formula 2.15 and formula 2.16 to heat and electric current dissipation processes yields the following basic equations of thermoelectricity¹²⁻¹⁴:

$$E_i = \rho_{ik} j_k + \alpha_{im} (\partial T / \partial x_m), \quad q_l = \Pi_{lk} j_k - \kappa_{lm} (\partial T / \partial x_m) \quad (2.17)$$

The first of relations given in Equation 2.17 is often written as

$$j_i = \sigma_{ik} E_k - \sigma_{ik} \alpha_{km} (\partial T / \partial x_m) \quad (2.18)$$

In Equation 2.17 and Equation 2.18, E_i is component of electric field intensity, ρ_{ik} are components of electric resistivity tensor, σ_{ik} are components of electric conductivity tensor, q_l is the component of heat flow density vector, j_k is the component of electric current density vector, κ_{lm} is the component of thermal conductivity tensor, x_m are Cartesian coordinates, indexes i, k, l, m run the values 1, 2, 3, the summation being done with respect to doubly encountered indexes.

Relations given in Equation 2.17 are called generalized Ohm's and Fourier laws.

As compared to conventional Ohm's law (Equation 2.15) and Fourier law (Equation 2.16), the generalized laws (Equation 2.17) include additional components comprising coefficients α_{ik} and Π_{ik} . These are the Seebeck and Peltier coefficients. Their physical meaning and relation to other kinetic coefficients will be considered below.

The Onsager principle (Equation 2.13) implies the following properties of kinetic coefficient tensors $\hat{\rho}$, $\hat{\kappa}$, $\hat{\alpha}$, $\hat{\sigma}$, $\hat{\Pi}$:

$$\sigma_{ik}(\mathbf{B}) = \sigma_{ki}(-\mathbf{B}), \rho_{ik}(\mathbf{B}) = \rho_{ki}(-\mathbf{B}), \kappa_{lm}(\mathbf{B}) = \kappa_{ml}(-\mathbf{B}), \alpha_{km}(\mathbf{B}) = (1/T) \Pi_{mk}(-\mathbf{B}) \quad (2.19)$$

For $\mathbf{B} = 0$ formulae 2.19 yield the following symmetry relations for tensors $\hat{\rho}$ and $\hat{\kappa}$:

$$\rho_{ik} = \rho_{ki}, \quad \kappa_{lm} = \kappa_{ml} \quad (2.20)$$

However, it should be borne in mind that tensor $\hat{\alpha}$, generally speaking, is not symmetrical even in the absence of a magnetic field.

2.3.2 Generalization of the Thomson Relations

The Thomson relations establish fundamental laws of relation between the Seebeck, Peltier, and Thomson effects. These relations are widely used in the theory of thermoelements and in the calculation of their parameters (efficiency, coefficient of performance, irreversible losses through caloric thermoelectric effects, etc.).

The formulation of the Thomson relations has experienced essential evolution. These relations were first established by Thomson¹ based on the use of classical thermodynamics of equilibrium reversible processes and looked at as a relation between the Peltier and Seebeck coefficients (the first Thomson relation [Equation 2.3]) and a relation between the Thomson and Seebeck coefficients (the second Thomson relation [Equation 2.4]) for isotropic media.

As indicated above, classical thermodynamics of reversible equilibrium processes is not quite correct for thermoelectric phenomena, so it was natural to study the Thomson relations based on the thermodynamics of irreversible processes after its fundamentals had been created by Onsager.⁸ This work was performed by Domenicali¹¹ and Samoilovich and Korenblit [12]. Nevertheless, the employment of the theory of irreversible processes did not change the expression of the Thomson relations (Equation 2.3 and Equation 2.4).

The reason for this is that the Seebeck, Peltier, and Thomson effects as such, although always accompanied by nonequilibrium electric conductivity and thermal conductivity processes, in the isotropic medium in a steady-state can be regarded as "quasi-equilibrium" and "quasireversible" in the sense that under these conditions their contribution to local entropy change \dot{s} of unit volume is zero.

On substituting into Equation 2.21 heat flow vector from Equation 2.17 we get

$$\dot{s} = -\text{div } \kappa \nabla \ln T + \rho j^2 / T \quad (2.21)$$

From Equation 2.22 it can be seen that in this case the unit change of entropy is determined only by two nonthermoelectric medium parameters, i.e., thermal conductivity and electric resistivity. Therefore, if we consider by convention only thermoelectric phenomena, abstracting from the

accompanying nonequilibrium processes of electric conductivity and thermal conductivity, the second law of thermodynamics for thermoelectric components of processes under study can be used as a strict equality $ds = -\text{div } \mathbf{q}/T$, valid for equilibrium processes instead of inequality $ds > -\text{div } \mathbf{q}/T$ of nonequilibrium thermodynamics.

Thus, a deeper insight into the Thomson relations in the first stage of thermodynamics of irreversible processes application to thermoelectricity did not culminate in the specification or establishment of new regularities.

The authors of Ref. [13] formulated the Thomson relations for the anisotropic media and the presence of a magnetic field. The relations generalized for this case took the form

$$\hat{H}(\mathbf{B}) = T\hat{\alpha}(-\mathbf{B}) \quad (2.22)$$

$$\hat{\tau}_T(\mathbf{B}) = T[\partial \hat{\alpha}(-\mathbf{B})/\partial T] \quad (2.23)$$

where the tilde sign signifies tensor transposition.

Another generalization of the Thomson relations, different from Equation 2.22 and Equation 2.23, was proposed in Ref. [14]. The necessity and content of this generalization lies in the following.

As can be seen from Equation 2.22 and Equation 2.23, the right-hand and left-hand tensors in these relations differ in the transposition and sign of vector \mathbf{B} . Therefore, physically Equation 2.22 and Equation 2.23 are formal statements on the equality of values belonging to two absolutely different physical states of medium. The first state (left-hand side of equalities) is characterized by a certain orientation of external influence vectors \mathbf{j} , \mathbf{q} (or ∇T) and \mathbf{B} , superimposed on the medium. The second state (right-hand side of equalities) is different in that vector \mathbf{j} here is oriented as vector \mathbf{q} of the first state; vector \mathbf{q} here is oriented as vector \mathbf{j} of the first state, and magnetic field \mathbf{B} reversed its direction. Thus, directly from Equation 2.22 and Equation 2.23, a relationship between the Seebeck, Peltier, and Thomson coefficients for one certain physical state of medium is not established, unlike the original Thomson formula given in Equation 2.3 and Equation 2.4.

Therefore, let us introduce into our consideration the local Peltier, Seebeck, Thomson, electric resistivity, and thermal conductivity coefficients for an arbitrary, but quite certain orientation of vectors \mathbf{j} , ∇T , \mathbf{q} , and \mathbf{B} and reformulate the Thomson relations in these terms. These coefficients are of the form

$$\rho^* = \mathbf{j}_0(\hat{\rho} \mathbf{j}_0), \quad \kappa^* = \mathbf{t}_0(\hat{\kappa} \mathbf{t}_0), \quad \tau^* = \mathbf{j}_0(\hat{\tau} \mathbf{t}_0), \quad \alpha^* = \mathbf{t}_0(\hat{\alpha} \mathbf{j}_0), \quad \Pi^* = \mathbf{t}_0(\hat{\Pi} \mathbf{j}_0) \quad (2.24)$$

where \mathbf{t}_0 and \mathbf{j}_0 are unit vectors of temperature gradient and electric current density.

Let us find a new form of the first Thomson relation.

Let us consider coefficient Π^* to the product α^*T with regard for Equation 2.22:

$$\alpha^*T = T\mathbf{t}_0(\hat{\alpha} \mathbf{j}_0) = \Pi^*\delta \quad (2.25)$$

where

$$\delta = \alpha^*(\mathbf{B})/\alpha^*(-\mathbf{B}) \quad (2.26)$$

A dimensionless parameter δ can be represented as

$$\delta(\mathbf{j}_0, \mathbf{t}_0, \mathbf{B}) = \mathbf{j}_0\hat{\alpha}(\mathbf{B})\mathbf{t}_0/\mathbf{j}_0\hat{\alpha}(-\mathbf{B})\mathbf{t}_0 \quad (2.27)$$

whence it is seen that this parameter in the absence of a magnetic field

$$\delta(\mathbf{j}_0, \mathbf{t}_0, 0) = 1 \quad (2.28)$$

In the presence of a magnetic field δ can be a value different from unity only in the case when

$$\hat{\alpha}(\mathbf{B}) \neq \hat{\alpha}(-\mathbf{B}) \quad (2.29)$$

This is possible if a magnetic field reversal causes a change in the Seebeck coefficients (Umkehr effect in low-symmetry crystals), whereby

$$-1 < \delta \leq 1 \quad (2.30)$$

from (3.10). With regard for thermodynamic limits for δ (3.15) it is evident that

$$\Pi^* \geq \alpha^* T \quad (2.31)$$

Thus, in the general case in the presence of a magnetic field in low-symmetry crystals a new form of relation (Equation 2.31), in contrast to Equation 2.3, takes the form of inequality. Only for the isotropic medium Equation 2.31 takes the form of absolute Thomson equality (Equation 2.3).

Equation 2.31 is a new form of the first Thomson relation.

Let us use the above approach for the second Thomson relation as well.

Dividing the Thomson and Seebeck tensors into symmetrical and nonsymmetrical, as well as even and odd components, from Equation 2.23 we get

$$\tau^* = T(\partial \alpha^{*+}/\partial T) - T(\partial \alpha^{*-}/\partial T) - 2\alpha^{*-} \quad (2.32)$$

where

$$\alpha^{*+} = \mathbf{t}_0(\hat{\alpha}^+ \mathbf{j}_0), \quad \alpha^{*-} = \mathbf{t}_0(\hat{\alpha}^- \mathbf{j}_0) \quad (2.33)$$

Equation 2.33 is a new form of the second Thomson relation.

In contrast to Equation 2.23, it comprises two odd with respect to magnetic field components $-T(\partial \alpha^{*-}/\partial T) - 2\alpha^{*-}$. In so doing, the presence of $-2\alpha^{*-}$ component allows for the existence of an odd Thomson effect in a medium where thermoemf is temperature independent.

Thus, a new form of the Thomson relations yields two essential results, namely the inequality $\Pi^* \geq \alpha^* T$ and the Thomson effect odd with respect to a magnetic field.

2.3.3 Thermodynamics of Caloric Effects in Thermoelectricity

The value of heat release rate Q in the anisotropic medium can be represented as

$$Q_j = -\text{div}(\mathbf{w}) - \text{div} \hat{\kappa} \nabla T \quad (2.34)$$

where energy flow vector is determined by the expression

$$\mathbf{w} = -\hat{\kappa} \nabla T + \hat{I} \mathbf{j} + (\bar{\mu}/e) \mathbf{j} \quad (2.35)$$

$\bar{\mu}$ is electrochemical potential of current carriers, e is their charge, and $\hat{\kappa}$ is the thermal conductivity tensor. Expression 2.34 with regard for Equation 2.35 can be rearranged as

$$Q_j = Q_{II} + Q_T + Q_B + Q_Y \quad (2.36)$$

where Q_{II} is the Peltier heat, Q_T is the Thomson heat, Q_B is the Bridgman heat, and Q_j is the Joule heat determined by the relations

$$Q_{II} = -T \mathbf{j} \{ \text{Div}_T(\hat{\alpha}^{s+} - \hat{\alpha}^{s-}) - \text{rot}(\mathbf{N}^+ - \mathbf{N}^-) \} \quad (2.37)$$

$$Q_T = -T \mathbf{j} \{ \partial(\hat{\alpha}^{s+} - \hat{\alpha}^{s-})/\partial T - 2\alpha^{s-} \} \nabla T - T \{ \partial(\mathbf{N}^+ - \mathbf{N}^-)/\partial T - 2\mathbf{N}^- \} [\nabla T \times \mathbf{j}] \quad (2.38)$$

$$Q_B = -T \text{Dev}(\hat{\alpha}^{s+} - \hat{\alpha}^{s-})/\text{Def} \mathbf{j} - T(\mathbf{N}^+ - \mathbf{N}^-) \text{rot} \mathbf{j} \quad (2.39)$$

$$Q_Y = \mathbf{j} \hat{\rho}^s \mathbf{j} \quad (2.40)$$

TABLE 2.1 Caloric Thermoelectric Effects

Name	Effect Type		Specific Heat Production
Peltier effect	Divergent	Even	$-T\mathbf{j}\text{Div}_T\hat{\alpha}^{s+}$
		Odd	$T\mathbf{j}\text{Div}_T\hat{\alpha}^{s-}$
	Eddy	Even	$T\mathbf{j}\text{rot}\mathbf{N}^+$
		Odd	$-T\mathbf{j}\text{rot}\mathbf{N}^-$
Bridgman	Deviation	Even	$-T\text{Dev}(\hat{\alpha}^{s+}) : \text{Def } \mathbf{j}$
		Odd	$T\text{Dev}(\hat{\alpha}^{s-}) : \text{Def } \mathbf{j}$
	Eddy	Even	$-T\mathbf{N}^+ \text{rot } \mathbf{j}$
		Odd	$T\mathbf{N}^- \text{rot } \mathbf{j}$
Thomson effect	Longitudinal	Even	$-T\mathbf{j} \frac{\partial}{\partial T}(\hat{\alpha}^{s+})\tau$
		Odd	$T\mathbf{j} \left(\frac{\partial \hat{\alpha}^{s-}}{\partial T} - 2\hat{\alpha}^{s-} \right) \tau$
	Transverse	Even	$-T \left(\mathbf{j} \frac{\partial}{\partial T}(\hat{\alpha}^{s+})\tau - \frac{\partial}{\partial T}\mathbf{N}^+[\tau\mathbf{j}] \right)$
		Odd	$\mathbf{j} \left(\frac{\partial \hat{\alpha}^{s-}}{\partial T} - 2\hat{\alpha}^{s-} \right) \tau + \left(T \frac{\partial \mathbf{N}^-}{\partial T} - 2\mathbf{N}^- \right) [\tau\mathbf{j}]$

In Equation 2.36 through Equation 2.40, $(\text{Div}_T \hat{t})_i = (\partial t_{ij}/\partial x_j)_{T=\text{const}}$, $(\text{Dev } \hat{t})_{ij} = t_{ij}^s - (\delta_{ij}/3)\text{Sp } \hat{t}^s$, $(\text{Def}_T \hat{t})_{ij} = 1/2(\partial j_i/\partial x_j + \partial j_j/\partial x_i)$, colon signifies a biscalar product of tensors. The formulae for heat release rate are summarized in Table 2.1. From the table it is evident that essential importance for caloric effects is assumed by spatial derivatives of these vectors, as well as by gradients of tensor components $\hat{\alpha}^{s\pm}$, resulting in new effects missing from classical theory.

2.3.4 Local and Integral Efficiency of Thermoelements

There are two approaches with two models developed for the description of thermoelements.

The first, most illustrative, approach is the integral approach. This approach utilizes concrete models of thermoelements as thermoelectric power converters. For example, a model of a thermocouple element was employed by Ioffe.¹⁵ A model of thermomagnetic power converter was used by Harman and Honig.¹³ Such models are based on concrete variants of heat exchange between power converter, heat sources, and heatsinks, as well as the matching of thermoelement resistance with an external electric circuit wherein the mode of maximum efficiency or maximum electric power is attained. Under this approach the expressions for efficiency could be derived only for the few simplest cases. In general, the problem of efficiency determination is very complicated, and its general solution has not been obtained so far because of its awkwardness with account of temperature dependences of material properties, optimal configuration of thermoelements, and other peculiarities of thermoelements and their operating conditions.

Therefore, the local approach is more productive than the integral one (Figure 2.1).

This approach to efficiency calculation was proposed by Zener¹⁶ and developed in Ref. [17] for thermomagnetic elements. Under this approach, parameters and properties of the thermoelectric energy conversion process in question are determined for the infinitesimal volume of thermoelement working medium. Then, if necessary, a change-over to integral parameters is made.

In Ref. [14] this approach was used to create a generalized local thermoelement model suitable for materials with arbitrary anisotropy in the presence of a magnetic field and deformations. Let us consider this model in more detail.

Figure 2.1 shows an infinitesimal volume dV of thermoelectric material. It is located between two isothermal surfaces with temperatures T and $T + dT$. The lateral surface of volume dV is adiabatically isolated. A quantity of heat dQ_h comes through the surface $T + dT$ into the middle of the volume. Heat flow density on the surface $T + dT$ is equal to \mathbf{q}_h . In the volume d there is thermal into electric energy conversion, resulting in electric current generation of density \mathbf{j} . A quantity of heat dQ comes through the

surface T of volume dV . Thus, the spent quantity of heat is dQ_h , and the resulting electric energy in conformity with the law of conservation of energy is $dQ_h - dQ_c$. Let us introduce the efficiency of thermoelectric energy conversion in volume d (local efficiency):

$$\eta_{\text{local}} = dQ_h - dQ_c / dQ_h \quad (2.41)$$

For its calculation it is advisable to introduce dimensionless parameters: dimensionless current $\mathbf{i} = \Pi^* \mathbf{j} / \kappa^* t$, dimensionless electric field $\mathbf{e} = \Pi^* \mathbf{E} / \rho^* \kappa^* t$, and dimensionless heat flow $\mathbf{k} = \mathbf{q} / \kappa^* t$, where t, j are modules of vectors ∇T and \mathbf{j} .

Then Ohm's and Fourier laws can be represented in a dimensionless form:

$$\mathbf{e} = \hat{R} \mathbf{i} + Z^* T \hat{A} \mathbf{t}_0 \quad (2.42)$$

$$\mathbf{k} = \hat{\pi} \mathbf{i} - \hat{\Theta} \mathbf{t}_0 \quad (2.43)$$

with introduced tensors of material constants — dimensionless thermoemf $\hat{A} = \hat{a} / \alpha^*$, dimensionless resistivity $\hat{R} = \hat{\rho} / \rho^*$, dimensionless thermal conductivity $\hat{\Theta} = \hat{\kappa} / \kappa^*$, and dimensionless Peltier coefficients $\hat{\pi} = \hat{\Pi} / \Pi^*$.

Expression (2.26) can be transformed as

$$\eta_{\text{local}} = \eta_{\text{Carnot}} (\rho^* j^2 + \alpha^* j t / \Pi^* t j - t^2) = \eta_{\text{Carnot}} \delta^{-1} (1 + (i / Z^* T) i - 1) \quad (2.44)$$

where η_{Carnot} is the Carnot efficiency of a local model, and parameter δ is determined by formula (2.11). Formula (2.29) takes into consideration a new parameter:

$$Z^* T = \alpha^* \Pi^* / \kappa^* \rho^* \quad (2.45)$$

As can be seen from Equation 2.44, the local efficiency is a function of three factors, namely the Carnot efficiency, the operating mode of thermoelement determined by a dimensionless current i , and the value $Z^* T$ that for given temperature T is determined by the properties of thermoelement material and the magnetic field.

Dependence η_{local} on dimensionless current (Figure 2.3) has maximum $\eta_{\text{local}}^{\text{max}}$ at

$$i = i_{\text{opt}} = \sqrt{1 + Z^* T} - 1 \quad (2.46)$$

and the value of this maximum efficiency is

$$\eta_{\text{local}}^{\text{max}} = \eta_{\text{Carnot}} Z e^* \quad (2.47)$$

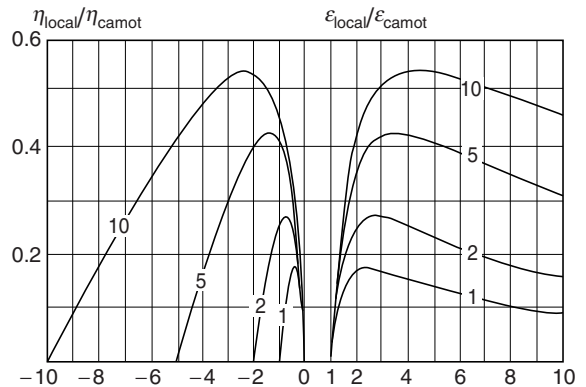


FIGURE 2.3 Local efficiency η_{local} and coefficient of performance ϵ_{local} vs. dimensionless current for various $Z^* T$ values.

introducing a new parameter

$$Ze^* = \delta \left(\sqrt{1 + Z^*T} - 1 / \sqrt{1 + Z^*T} + 1 \right) \quad (2.48)$$

Let us elucidate physical content of parameters Ze^* and Z^*T .

As is evident from Equation 2.47, parameter Ze^* indicates the portion of the Carnot efficiency that can be obtained in local efficiency with the use of given thermoelectric material. Formula (2.36) implies that the generalized thermoelectric efficiency Z^*T is the only parameter to determine Ze^* ; hence the local efficiency for given material at temperature T . Ze^* as a function of Z^*T is shown in Figure 2.4.

From the figure it can be seen that at $Z^*T \rightarrow \infty$ the efficiency of thermoelectric converter tends to the efficiency of the Carnot cycle.

To go from the local efficiency η_{local} to the integral efficiency η_{integral} , it is necessary in a thermoelectric energy converter to integrate the local efficiencies for all infinitesimal dV volumes along current lines. This integration can be replaced by integration with respect to temperature T .

Then

$$\eta_{\text{integral}}^{\text{max}} = 1 - \exp(-S_z) \quad (2.49)$$

where

$$S_z = \int_{T_1}^{T_2} Ze^* d \ln T \quad (2.50)$$

Graphically, the integral is depicted as area S_z of a hatched curvilinear trapezoid under the curve of Ze^* versus $\ln T$ plot (Figure 2.5). The larger this area is, the higher is the integral efficiency of conversion.

Parameters similar to Ze^* and Z^*T for partial cases of several thermoelement types are well known in the theory of thermoelements. Thus, in classical work by A.F. Ioffe,¹⁵ from the consideration of an integral model of thermocouple thermoelement parameters were introduced to estimate the quality of materials used in thermocouple thermoelements, namely, the thermoelectric figure-of-merit of isotropic materials

$$Z = \alpha^2 \sigma / \kappa \quad (2.51)$$

having dimensions of the inverse temperature and a dimensionless parameter of thermoelectric figure-of-merit (Ioffe criterion) for such materials:

$$I_o = ZT \quad (2.52)$$

The isotropic materials are characterized by quality criterion also introduced by Zener:

$$Ze = \sqrt{1 + ZT} - 1 / \sqrt{1 + ZT} + 1 \quad (2.53)$$

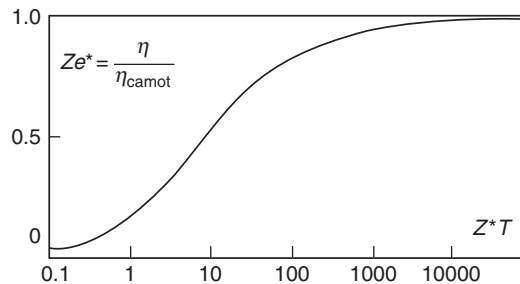


FIGURE 2.4 Ze^* as a function of Z^*T .

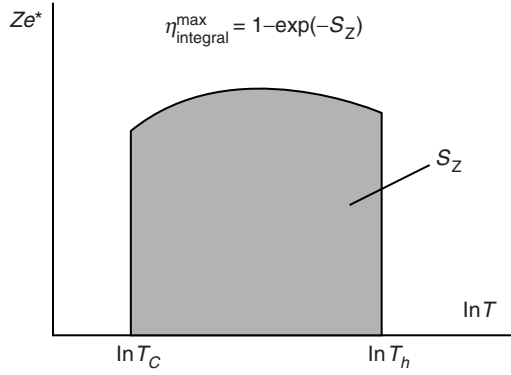


FIGURE 2.5 Calculation of integral efficiency as $S_Z = \int_{T_C}^{T_h} Ze^* d \ln T$.

It is readily apparent from Equations 2.33, 2.36, 2.37, and 2.38 that the well-known Ioffe and Zener criteria are partial cases of parameters Z^*T and Ze^* . Thus, for example, for the isotropic medium from Equation 2.32 we get the efficiency of thermocouple element

$$\eta = \eta_{\text{Carnot}}(M - 1)/(M + T_c/T_h) \quad (2.54)$$

where

$$M = \sqrt{1 + 1/2(Z_0(T_c + T_h))} \quad (2.55)$$

$$Z_0 = (\alpha_1 - \alpha_2)^2/(\sqrt{\kappa_1\rho_1} + \sqrt{\kappa_2\rho_2}) \quad (2.56)$$

is an optimal thermoelectric figure-of-merit of thermoelement, α , ρ , and κ with the respective indexes are thermoelectric coefficient, electric resistivity, and thermal conductivity, accordingly, of the first and second thermocouple legs.

For the efficiency of the well-known anisotropic thermoelement from Equation 2.47 we also get the expression which coincides with Equation 2.54, but in this case $M = \sqrt{1 + Z_{\perp}T^*}$, where $Z_{\perp} = (\Delta\alpha)^2/4\rho^*\kappa^*$, $\Delta\alpha$ is the difference in components of the thermo-EMF tensor, and T^* is the thermoelement temperature averaged along its gradient.

For the Nernst thermoelement we have a similar expression, but the anisotropy of thermoemf is caused by a magnetic field and characterized by the value $Q^{\perp}B$:

$$Z_{\perp} = (Q^{\perp}B)^2/\rho^*\kappa^* \quad (2.57)$$

where Q^{\perp} is the Nernst–Ettingshausen transverse coefficient.

It is evident that parameters Z^*T and Ze^* comprise the well-known Ioffe and Zener criteria as partial cases. However, they are more general and suitable for an arbitrary anisotropy of thermoelement material and an arbitrary magnetic field. Therefore, it is advisable to call Z^*T a generalized thermoelectric figure-of-merit, and accordingly, Ze^* a generalized Zener criterion.

The thermodynamic restrictions for the generalized criteria of efficiency and the Peltier and Seebeck coefficients are given in Table 2.2.

The generalized expressions (Equation 2.47 and Equation 2.49) for the local and integral efficiencies are the most universal and allow calculating the efficiency of thermoelements for any anisotropic and inhomogeneous medium in an arbitrary magnetic field.

TABLE 2.2 Thermodynamic Restrictions for Thermoelectric Parameters

Parameter	Name	Restriction	Remark
$I_0 = ZT$	Ioffe criterion	$0 \leq ZT < \infty$	For isotropic medium
Ze	Zener criterion	$0 \leq Ze^* < 1$	
Ze^*	Generalized Zener criterion	$0 \leq Ze^* < 1$	For media of any
Z^*T	Generalized thermoelectric figure-of-merit	$-1 \leq Z^*T < \infty$	symmetry and in the
Π^*, α^*	Generalized Peltier and Seebeck coefficients	$\Pi^* \geq \alpha^*T$	presence of a magnetic field

2.4 Conclusion

Modern thermodynamic theory of thermoelectricity based on the thermodynamics of irreversible processes:

- (i) Gives new forms as given in Equation 2.31 and Equation 2.32 of the Thomson relations.
- (ii) Establishes new generalized quality criteria (Equation 2.45 and Equation 2.48) for material used in thermoelectricity.
- (iii) Discovers new thermoelectric effects (Table 2.1).
- (iv) Allows, based on the local expressions for efficiency (Equation 2.44) and temperature distribution, calculating the integral efficiencies (Equation 2.49) for any thermoelements (Figure 2.5).

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